

High resolution nuclear magnetic resonance spectroscopy of highly-strained quantum dot nanostructures

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Much new solid state technology for single-photon sources¹, detectors^{2,3}, photovoltaics⁴ and quantum computation^{5,6} relies on the fabrication of strained semiconductor nano-structures. Successful development of these devices depends strongly on techniques allowing structural analysis on the nanometer scale. However, commonly used microscopy methods⁷⁻¹⁰ are destructive, leading to the loss of the important link between the obtained structural information and the electronic and optical properties of the device. Alternative non-invasive techniques such as optically detected nuclear magnetic resonance (ODNMR) so far proved difficult in semiconductor nano-structures due to significant strain-induced quadrupole broadening of the NMR spectra. Here, we develop new high sensitivity techniques that move ODNMR to a new regime, allowing high resolution spectroscopy of as few as 10^5 quadrupole nuclear spins. By applying these techniques to individual strained self-assembled quantum dots, we measure strain distribution and chemical composition in the volume occupied by the confined electron. Furthermore, strain-induced spectral broadening is found to lead to suppression of nuclear spin magnetization fluctuations thus extending spin coherence times. The new ODNMR methods have potential to be applied for non-invasive investigations of a wide range of materials beyond single nano-structures, as well as address the task of understanding and control of nuclear spins on the nanoscale, one of the central problems in quantum information processing¹¹⁻¹³.

Most nuclei used in optically active III-V semiconductor nanostructures possess non-zero quadrupole moments sensitive to electric field gradients caused e.g. by strain. Due to strong spectral broadening NMR on quadrupole nuclei is challenging even for macroscopic samples¹⁴⁻¹⁶. As a result control of nuclear spins using NMR has only been achieved in strain-free GaAs/AlGaAs semiconductor quantum dots (QDs)¹⁷⁻¹⁹. By contrast application of similar techniques to widely researched strained self-assembled quantum dots were limited to large ensembles of QDs, where quadrupole broadening lead to uncertainty in interpretation of the effects observed under radio-frequency (rf) excitation^{20,21}.

The new ODNMR spectroscopy technique we present is based on continuous-wave broadband rf excitation with specially designed spectral patterns, which for nuclei with spin I in strained structures provides sensitivity enhancement by a factor of $(I + 1/2)^3$ compared to conventional saturation NMR techniques previously used in unstrained nano-structures¹⁷⁻¹⁹. Such enhancement (particularly large for high spin nuclei such as $I=9/2$ indium) brings NMR to a qualitatively new level: it allows high resolution spectroscopy in individual few-nanometer-sized strained quan-

tum dots having only 10^4 - 10^5 nuclear spins which are subject to large inhomogeneous quadrupole broadening up to 20 MHz. To demonstrate the capabilities of this technique we use NMR spectra measured for InP/GaInP and InGaAs/GaAs QDs to estimate several key structural properties such as material composition, elastic strain magnitude and distribution in the volume sampled by the electron wave-function. Furthermore, using related techniques we find that spectral broadening caused by strain results in enhancement of the coherence of nuclear spins by a factor of 10 compared with unstrained structures, leading to coherence times of ≈ 2.5 ms.

In what follows we present results for two different types of strained semiconductor nano-structures: InP/GaInP and InGaAs/GaAs self-assembled quantum dots [for sample details see Supplementary Information (SI) Section S1]. All measurements were performed at $T = 4.2$ K, in external magnetic field B_z normal to the sample surface. Under excitation with circularly polarized light, nuclear spins become strongly polarized due to spin transfer from electrons via the hyperfine interaction²². The resulting nuclear spin polarization on the dot is detected in photoluminescence (PL) of excitons in single QDs as shown in Fig. 1(a) for InGaAs and in Fig. 1(b) for InP dots in high magnetic field $B_z > 5$ T. Each spectrum consists of an exciton Zeeman doublet with splitting E_z . Detection of changes in E_z allows measurement of the electron Overhauser shift^{2,22} proportional to the degree of nuclear polarization P_N . ODNMR measurements were carried out using the pump-probe method schematically shown in Fig. 1(c). The dot is first excited with a circularly polarized laser pulse of duration T_{pump} . After that the rf excitation is applied in the dark for duration T_{rf} . Finally a short (T_{probe}) laser pulse is applied to measure the PL spectrum and probe the effect of the rf field on nuclear polarization, which allows NMR signal to be obtained as the absolute magnitude of the Overhauser shift. More details of experimental methods can be found in SI Sec. S2.

The explanation of our method and its comparison with the "saturation" NMR techniques applied in strain-free materials^{17,18} is given in Fig. 2, using an example of spin $I = 5/2$ nuclei. In an external magnetic field B_z along the Oz axis nuclear spin levels experience Zeeman shifts $\propto B_z I_z$ determined by their spin projections I_z . The oscillating magnetic field B_{rf} perpendicular to Oz couples only spin levels with I_z differing by ± 1 . If the nucleus is subject to an electric field gradient (EFG) along the Oz axis (e.g. induced by elastic strain), in addition to the splitting induced by B_z , the energies of spin levels will change^{8,9} by a value proportional to I_z^2 (see SI Sec. S3), and all dipole active transitions will have different frequencies, as depicted in Fig. 2(b).

Let us consider an ensemble of nuclei with spins $I = 5/2$ all subject to the same EFG and polarized, so that $I_z = 5/2$ levels have higher population than $I_z = -5/2$. The probabilities p_{I_z}

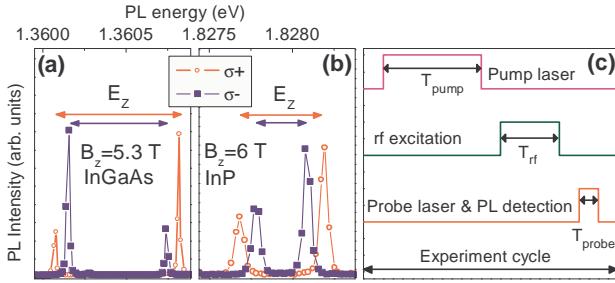


FIG. 1. (a) and (b) show typical photoluminescence spectra for InGaAs/GaAs (a) and InP/GaInP (b) quantum dots measured in magnetic field $B_z = 5.3$ and 6 T, respectively. Squares (circles) show PL spectra measured for $\sigma^{-(+)}$ excitation exhibiting differing Zeeman splittings E_z due to the nuclear spin polarization (anti-)parallel to B_z . (c) shows the timing diagram of the experimental cycle including optical pump and probe, and rf excitation. We use $T_{pump} = 4 \div 7$ s, $T_{rf} = 4 \div 6$ s and $T_{probe} = 3 \div 16$ ms.

to find a nucleus with spin I_z will depend on I_z as sketched by the solid lines in Fig. 2(c). The total nuclear spin polarization degree (which is detected optically) is $P_N = \sum_{k=-I}^I p_k \times k/I$, so that $|P_N| \leq 1$. Arrows in Fig. 2(c) indicate the maxima in the NMR spectrum in Fig. 2(b) corresponding to allowed transitions between adjacent pairs of nuclear spin levels.

In conventional "saturation" NMR spectroscopy, radio-frequency excitation at a frequency ν or, a distribution of frequencies with a width w_{exc} is applied [Fig. 2(a)]. P_N will only change in the case when ν is in resonance with a transition between I'_z and $I'_z + 1$ levels, for example, $-3/2 \leftrightarrow -1/2$ in Figs. 2(a-c). This occurs as the populations of these spin levels equalize under sufficiently long resonant rf excitation [dotted lines in Fig. 2(c)], which at the same time has no effect on populations of the other spin levels. As a result, the overall change in nuclear polarization is small, making the resonance difficult to detect.

Very major enhancement of the changes in P_N can be achieved by using an alternative approach developed in this work [see Fig. 2(d)]: we use broad band excitation with a continuum spectrum containing a gap of width w_{gap} . As the rf excitation spectrum in Fig. 2(d) is an inversion of that in Fig. 2(a), we introduce the term "inverse" spectroscopy. The effect of such excitation on the populations p_{I_z} is demonstrated in Fig. 2(f). If the gap is out of resonance with all transitions, all p_{I_z} are equalized (solid lines) and nuclear spin polarization is completely erased ($P_N = 0$). If, however, the gap is in resonance with the $I'_z \leftrightarrow I'_z + 1$ transition, i. e. one of the transitions is not excited, the equalization of populations occurs independently for two groups of levels with $I_z \leq I'_z$ or $I_z \geq I'_z + 1$ (dotted lines). Thus the resonance condition for one of the transitions affects the populations of all states including $I_z = \pm I$ states, which give the largest contribution to P_N .

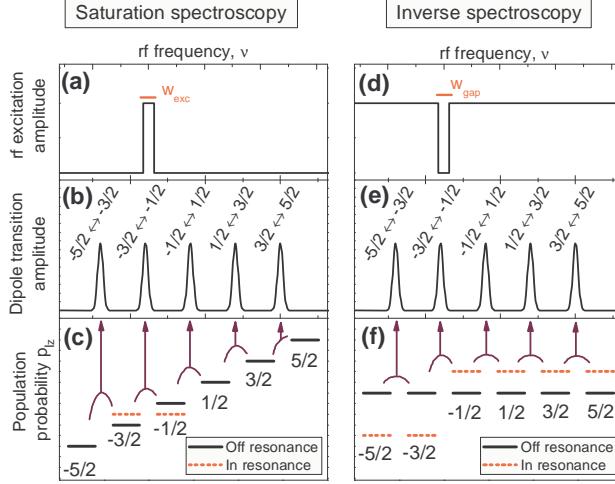


FIG. 2. Schematics explaining "saturation" (a)-(c) and "inverse" (d)-(f) NMR spectroscopy applied to quadrupolar nuclei. The case of an ensemble of spin-5/2 nuclei subject to the same electric field gradient is considered for clarity. (a) and (d) show rf excitation spectra in the two spectroscopy methods. Spectra of dipole transitions between the nuclear spin levels are shown in (b) and (e). (c) and (f) show population probabilities of the nuclear spin levels. Arrows show the transitions in the nuclear spectra in (b) and (e) corresponding to pairs of the spin states coupled by the rf field. Solid lines show the population probabilities for the case when the rf maximum in (a) and the gap in (d) are off resonance with all transitions. Dashed lines show the case when the maximum in (a) and the gap in (d) are in resonance with $-3/2 \leftrightarrow -1/2$ transition.

In the experiment, the "inverse" NMR spectrum is obtained by scanning the central frequency ν of the gap, while w_{gap} is chosen to control the balance between the spectral resolution and sensitivity (NMR signal amplitude). It is possible to show (see SI Sec. S4) that for "inverse" method the enhancement of the changes in nuclear polarization exceed $(I + 1/2)^3$ ($=125$ for spin $I = 9/2$) compared to the saturation NMR method in Fig. 2(a). This is a significant improvement compared to the existing "population transfer" technique where a maximum enhancement of $2I$ can be achieved¹⁶.

Fig. 3 shows a set of ODNMR spectra measured on single InP (a,b) and InGaAs (c-f) QDs at $B_z \approx 5.3$ T. In the nominally InP dots grown in GaInP barriers, the "inverse" technique allows to resolve contributions from quadrupole nuclei ^{115}In , ^{69}Ga and ^{71}Ga within the volume probed by a single electron. In Fig. 3(a) the ^{115}In peak dominating the spectrum, consists of a sharp central line [corresponding to $-1/2 \leftrightarrow 1/2$ central transition (CT)] with amplitude $\sim 40 \mu\text{eV}$ at ~ 49.7 MHz, and two broad bands of satellite transitions (STs) to lower and higher frequencies each stretching up to ± 7 MHz. These sidebands are due to strain-sensitive, quadrupole split transitions

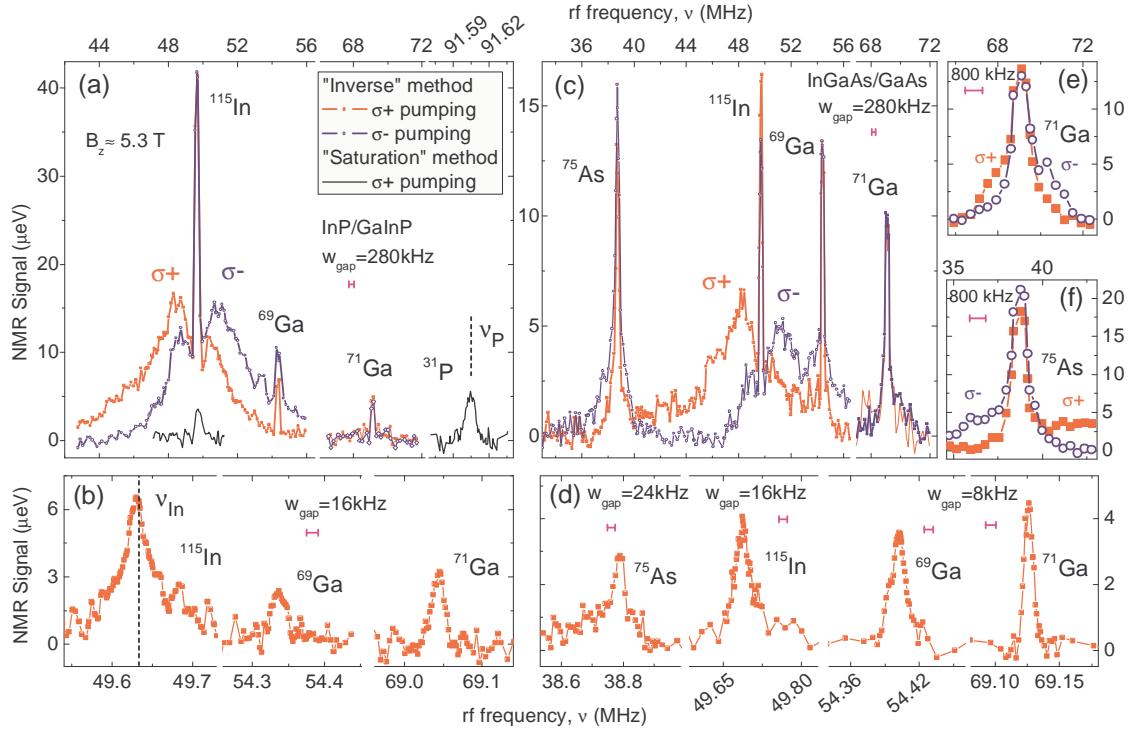


FIG. 3. ODNMR spectra measured at $B_z \approx 5.3$ T in self-assembled QDs using the "inverse" method with σ^+ (red curves) or σ^- (blue curves) optical pumping and using the "saturation" method with σ^+ pumping (black curves). (a) and (b) show ODNMR spectra for InP/GaInP dots measured with resolution $w_{gap} = 280$ kHz in (a) and 16 kHz in (b), and applying "saturation" spectroscopy with a width $w_{exc} = 450$ kHz for ^{115}In and single-frequency excitation for spin-1/2 ^{31}P in (a). (c)-(f) show ODNMR spectra for InGaAs/GaAs dots measured with resolution $w_{gap} = 280$ kHz in (c), 8-24 kHz in (d), and 800 kHz in (e,f). Vertical line in (b) shows indium frequency $\nu_{In} \approx 49633$ kHz corresponding to unstrained InP.

between spin levels with $|I_z| > 1/2$. The relative amplitudes of the side-bands reflect the initial alignment of the nuclear spins by circularly polarized excitation: the high (low) frequency band has a higher (lower) intensity for σ^- (σ^+) excitation. By contrast, with the saturation method applied to ^{115}In nuclei a weak line with amplitude ~ 3 μeV [see Fig. 3(a)] can be detected only for rf excitation width $w_{exc} = 450$ kHz or larger, i.e. at low resolution. For spin-1/2 ^{31}P nuclei unaffected by quadrupole effects the saturation method with monochromatic rf excitation reveals a single line with a width of ~ 8 kHz at $\nu_P \approx 91605$ kHz.

The ODNMR spectra of a InGaAs/GaAs QD measured using the "inverse" method ($w_{gap} = 280$ kHz) are shown in Fig. 3(c). Here the central transitions have similar amplitudes for the four isotopes present in the dot, revealing significant substitution of indium by gallium. Satellite transitions are observed only for spin-9/2 ^{115}In and have similar widths to the case of InP dots. In order

to observe these transitions for spin-3/2 nuclei we have carried out "inverse" NMR measurements with a larger $w_{gap}=800$ kHz as shown in Figs. 3(e) and (f) for ^{71}Ga and ^{75}As respectively. For ^{71}Ga the spectral range where STs are observed is within ± 2.5 MHz on both sides of the central line, whereas it is significantly broader for ^{75}As due to its larger quadrupole moment Q .

The structure of the central transitions is affected by strain only via weak second-order quadrupole interaction⁹. It is measured using "inverse" NMR with a smaller $w_{gap}=8 \div 24$ kHz to provide higher resolution. The smallest linewidth of ~ 8 kHz is observed for ^{71}Ga in InGaAs QDs while more sensitive to quadrupole interaction ^{75}As as well as ^{115}In in both materials have linewidths of ~ 40 kHz. Broadening of the CT line as well as its shift with respect to resonance frequency in unstrained bulk material [shown by vertical line in Fig. 3(b) for ^{115}In in InP] appear if electric field gradient direction deviates from that of magnetic field and thus reflect the distribution of elastic strain directions within the volume probed by the electron.

Quadrupole effects are insensitive to isotropic (hydrostatic) strain, but can provide information on biaxial and shear strains. For a given electron wavefunction and strain distribution within the QD it is possible to calculate an "inverse" NMR spectrum that can be directly compared with experiment. Since detailed quantum dot modeling²⁶ is beyond the scope of this work we limit our discussion to some quantitative estimates. For example, it is observed in Figs. 3 (a,c) that satellite transitions $I'_z \leftrightarrow I'_z + 1$ of ^{115}In corresponding to different I'_z are not resolved. This signifies a strong variation of the quadrupole shifts over the volume of the dot resulting from the variation of elastic strain. In particular, it can be seen that ST bands have non-zero amplitudes at the CT frequency, implying that for some nuclei the quadrupole splitting is zero. This can be explained by relaxation of the biaxial strain near the center of the dot as predicted by model calculations^{14,15}. On the other hand, the maximum values of the biaxial strain can be readily estimated from the maximum frequency shifts observed for the STs. For the spin-3/2 ^{71}Ga , the largest shift of the STs from the CT in InGaAs/GaAs QDs is ~ 2.5 MHz [Fig. 3(e)]. Using the values of the EFG-elastic tensor measured in bulk GaAs¹² this allows the maximum biaxial strain with principle axis along Oz to be estimated as $|\epsilon_b| \sim 6\%$. This is somewhat smaller than the maximum $|\epsilon_b| \sim 9 \div 15\%$ predicted for interfacial regions of InAs dots of different shapes¹⁵, possibly a signature of "smoothing" of the interface between the dot and the barrier due to interdiffusion. Using NMR on ^{115}In we find in a similar way the maximum strain for InP/GaInP dots of $|\epsilon_b| \sim 5\%$. (See details in SI Sec. S6).

The NMR data in Fig. 3 can be used to estimate relative gallium and indium concentrations ρ_{Ga} and ρ_{In} . For InGaAs dots in Fig. 3(c) similar CT signals are observed for ^{71}Ga and ^{115}In isotopes. However, we need to take into account, that for the ^{115}In isotope the NMR signal is

enhanced due to the larger nuclear magnetic moment of indium $\mu_{(115In)}/\mu_{(71Ga)} \approx 2$, and its larger natural abundance ($\sim 96\%$) compared to 40% for ^{71}Ga . In this way we estimate $\rho_{In} \approx 20\%$ and $\rho_{Ga} \approx 80\%$ for InGaAs dots. Similar estimates for InP dots give $\rho_{In} \approx 65\%$ and $\rho_{Ga} \approx 35\%$. These estimates are further confirmed by more detailed measurements and analysis presented in SI Sec. S5 .

The spectral widths exceeding 10 MHz observed for spectra in Fig. 3 are due to inhomogeneous quadrupole broadening. However, each nuclear spin transition has a finite intrinsic linewidth w_{nuc} determined by fluctuations of the local fields, created by neighboring nuclear spins. In unstrained structures w_{nuc} can be determined by spin-echo techniques¹⁹, using π and $\pi/2$ rf-pulses for coherent manipulation of nuclear spins. In strained structures uniform excitation of nuclear spins, with spectral dispersion of several MHz, would require very short rf-pulses, which in turn require rf-powers that are difficult to achieve with available hardware¹⁵. However, as we now show, nuclear spin coherence can be probed using an alternative approach based on low-power continuous-wave rf excitation with a special spectral pattern.

This approach is demonstrated in Fig. 4 for InP QDs. We measure the rate R_{rf} of nuclear spin depolarization induced by broad-band rf excitation consisting of equally spaced spectral modes [rf spectra are sketched with solid lines in Figs. 4 (b,c)]. The measurements are carried out for different spacings w_m between the modes, while keeping a constant spectral range 44-47.5 MHz corresponding to the satellite transitions of In nuclei [see Fig. 3(a)] and constant total power of the rf excitation.

The strong reduction of R_{rf} with increasing w_m observed in the experiment [Fig. 4(a)] is qualitatively explained in Figs. 4(b,c). For $w_m < w_{nuc}$ [Fig. 4(b)] the discrete structure of the rf-spectrum is averaged out by the broadening of the nuclear spin transition and each nuclear spin transition is excited by many modes resulting in fast depolarization. If the mode spacing is increased ($w_m > w_{nuc}$) there is a high probability that a given nuclear spin transition is out of resonance with all modes [Fig. 4(c)]. Strong suppression of R_{rf} observed experimentally at $w_m \approx 4$ kHz [Fig. 4(a)] will take place for very large mode spacing $w_m \gg w_{nuc}$ when most of the nuclear transitions will be out of resonance with rf excitation. Model fitting allows an intrinsic linewidth $w_{nuc} \approx 0.13$ kHz to be determined. Furthermore, analysis of the lineshape of individual nuclear spin transitions reveals a deviation from a Lorenzian lineshape indicative of non-exponential dynamics of the transverse nuclear magnetization (see details in SI Sec. S7).

From w_{nuc} we can estimate the nuclear spin decoherence time of indium nuclei as $T_2 \approx 1/(\pi w_{nuc}) \approx 2.5$ ms. This exceeds by nearly an order of magnitude previously reported T_2 for

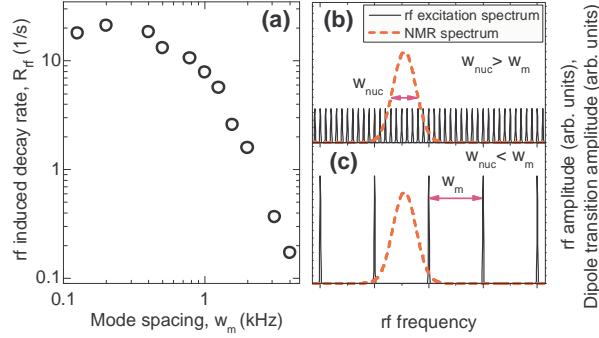


FIG. 4. (a) Experimental dependence of rf induced nuclear depolarization rate R_{rf} on the spacing w_m between spectral modes of the rf excitation. (b) and (c) qualitatively explain the effect of the variation of w_m on the nuclear polarization decay rate (see text). Solid and dashed lines show schematically spectra of rf excitation and nuclear spin dipole transition, respectively.

quadrupole nuclei in unstrained GaAs/AlGaAs QWs³⁰ (0.27 ms) and QDs¹⁹ (0.35 ms). This can be interpreted as a result of large quadrupole shifts, caused by inhomogeneous elastic strain, that make flips of spin states with $|J_z| > 1/2$ energetically forbidden, partially freezing fluctuations of the dipole-dipole field. The nuclear spin decoherence time is likely to be determined by spin flips of the $-1/2 \leftrightarrow 1/2$ transition of both quadrupole nuclei and phosphorus. Thus, while leading to inhomogeneous spectral broadening exceeding 10 MHz, quadrupole interaction has the beneficial effect of narrowing of individual transitions down to $w_{nuc} \approx 0.13$ kHz.

The proposed techniques may become a useful tool in development of single QDs for experiments on electron and hole spin coherence, as direct measurements of material properties such as composition and strain have now been made possible. This will potentially allow a generation of semiconductor nano-structures with tailored material properties for these applications. Furthermore, our experiments reveal very robust coherence properties of nuclear spins in strained structures, showing that introduction of strain is one of the ways to achieve a very stable nuclear spin bath, which is of potential significance for enhancing electron and hole coherence on the nanoscale. Finally, we note that these techniques may be applicable in a wide range of NMR detection schemes and structures beyond quantum dots. One of the challenges will be to develop nano-NMR techniques (including imaging) sensitive to yet smaller numbers of nuclei in the solid state environment.

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AUTHOR CONTRIBUTIONS A.B.K. and M.H. developed and grew the samples. A.M.S. and R.B. produced TEM images of QDs. J.P. processed the samples. E.A.C. and A.I.T. conceived the experiments. E.A.C. developed new techniques and carried out the experiments. E.A.C., K.V.K., A.D.A. and A.I.T. analyzed the data. E.A.C., A.I.T. and M.S.S. wrote the manuscript with input from all authors.

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SUPPLEMENTARY INFORMATION

In this document we refer to the figures 1-4 of the main text as well as to supplementary figures S1-S5.

The document consists of the following sections:

- S1. Details of sample structure and growth,
- S2. Details of experimental techniques,
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S1. DETAILS OF SAMPLE STRUCTURE AND GROWTH

We use InP/GaInP self-assembled quantum dots (QDs) grown by metal-organic vapor-phase epitaxy (MOVPE) and InGaAs/GaAs quantum dots grown by molecular beam epitaxy (MBE). Both samples are not intentionally doped and have no electric gates.

The InP/GaInP sample^{S1,S2} was grown in a horizontal flow quartz reactor using low-pressure MOVPE on (100) GaAs substrates misoriented by 3° towards ⟨111⟩. The growth temperature of the GaAs buffer and bottom $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ layer was 700° C. Before proceeding to the deposition of InP and the $\text{Ga}_{0.5}\text{In}_{0.5}\text{P}$ capping layer, the wafer was cooled to 650° C. The grown GaInP layers were nominally lattice matched to GaAs. A low InP growth rate of 1.1 Å/s and deposition time of 10 seconds were chosen.

The InGaAs/GaAs sample^{S3-S5} consists of a single layer of InAs quantum dots (QDs) placed within a microcavity structure which is used to select and enhance the photoluminescence from part of the inhomogeneous distribution of QD energies. The sample has been produced using a single step MBE process and consists of a GaAs cavity of thickness λ/n formed between an asymmetric set of distributed Bragg reflector pairs, which uses 16 pairs of $\text{GaAs}/\text{Al}_{0.8}\text{Ga}_{0.2}\text{As}$ distributed Bragg reflector pairs below and 6 pairs above the cavity. The resulting cavity Q factor is ~ 250 and the cavity has a low temperature resonant wavelength at around 920 nm. The luminescence of the

QDs is further enhanced by the presence of a GaAs/AlAs short-period superlattice surrounding the QD layer. The superlattice and DBR layers are grown around 620° C. The quantum dots were formed by deposition of 1.85 monolayers (MLs) of InAs at a growth temperature of 510° C and a growth rate of 0.1 ML/s. The deposition amount is just above that required for the nucleation of QDs (\sim 1.65 ML) but is well below the amount required to produce a mature QD distribution. As a result, we obtain a low density of infant QDs at the post-nucleation stage, which are small and have a low concentration of indium.

Both QD samples were examined using transmission electron microscopy (TEM). Fig. S1 shows images for InP/GaInP (a-b) and InGaAs/GaAs (c-e) samples taken under dark field 002 condition, which gives compositionally-sensitive diffraction contrast^{S6}. We find that InP dots are disk shaped with lateral size of \sim 75 nm and a height of \sim 4.5 nm. Images taken on the InGaAs/GaAs sample clearly show the AlGaAs layers of the Bragg mirror and the superlattice as well as pyramidal shaped QDs approximately 30 nm wide at their base and 5 nm high in the center.

S2. DETAILS OF EXPERIMENTAL TECHNIQUES

The experiments are performed with the sample placed in an exchange-gas cryostat at $T = 4.2$ K, and using an external magnetic field B_z normal to the sample surface. In order to detect nuclear polarization on the dot we use high resolution micro-photoluminescence (PL) spectroscopy of single QDs (see experimental setup scheme in Fig. S2). The QD PL is excited by a laser resonant with the wetting layer states ($E_{exc}=1.88$ eV for InP dots and $E_{exc}=1.46$ eV for InGaAs dots) and analyzed with a 1 meter double spectrometer coupled to a CCD. Manipulation and probing of

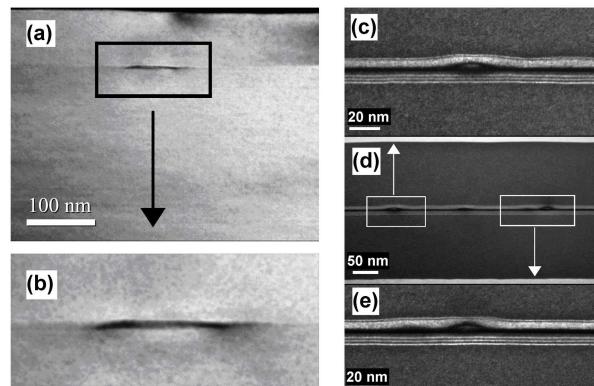


FIG. S1. Transmission electron microscope (TEM) images showing the structure of InP/GaInP (a-b) and InGaAs/GaAs (c-e) QDs. (b) shows zoomed part of the image in (a), (c) and (e) are zoomed parts of (d).

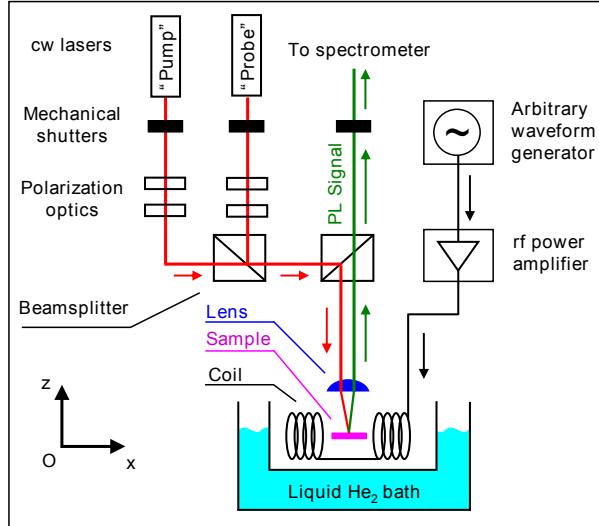


FIG. S2. Experimental setup. The sample is placed inside an insert filled with low-pressure helium gas with optical access from the top. The insert is immersed in a liquid helium bath cryostat. Photoluminescence (PL) is excited by diode lasers. All experiments are performed in the Faraday geometry with excitation and collection normal to the sample surface. Focusing of the laser and collection of PL from a QD are performed with an aspheric lens with focal length $f \approx 2$ mm and numerical aperture $NA \approx 0.5$. The collected PL signal is coupled via an optical fiber to the entrance slit of a double spectrometer with a charged coupled device (CCD) camera. Using line fitting or calculating center of mass it is possible to determine the shifts in QD PL energy as small as $1 \mu\text{eV}$. We use two identical lasers combined via a beamsplitter which allow independent control of power and polarization of "pump" and "probe" pulses. Mechanical shutters are used to control the light of both lasers and PL signal according to the pump-probe timing diagram [Fig. 1(c) of the main text]. Time accuracy of the shutters is ~ 1 ms. Magnetic field up to 8 T can be applied perpendicular to the sample surface (along the Oz direction). Oscillating radio-frequency (rf) magnetic field along the Ox direction is produced by two coils on each side of the sample. The rf signal is produced by digital arbitrary waveform generators with analog modulators, and after the power amplifier, coupled to the coil via a coaxial cable.

nuclear spin polarization relies on the hyperfine interaction of electrons and nuclear spins^{S7}, and requires polarization-resolved excitation and detection of light as described in the main text.

The waveform for the radio-frequency excitation is produced by a digital arbitrary waveform generator. "Inverse" spectroscopy with a continuous rf excitation spectrum shown in Fig. 2(d) requires an aperiodic signal, which can not be produced by a digital device. We thus approximate the spectrum shown in Fig. 2(d) with a spectrum consisting of a large number of discrete modes with equal spacing w_m (typically $w_m = 0.4$ kHz) as shown in Fig. S3. Since the rf signal has a finite power, it has to be limited in the spectral domain to a width w_{exc} (typically $w_{exc} = 20$ MHz). The

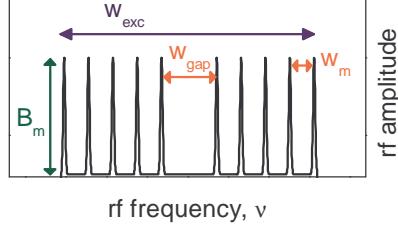


FIG. S3. Schematics of the spectrum of rf excitation. The spectrum has a total width w_{exc} up to 20 MHz and consists of many modes with equal amplitudes B_m and spacing w_m , which is varied in different measurements in the range 0.1 \div 4 kHz ($w_m = 0.4$ kHz is used for "inverse" spectroscopy). For "inverse" NMR spectroscopy the spectrum can also have a gap in the center with a width w_{gap} varied in the range 8-800 kHz.

signal waveform is synthesized to have no spectral components within a gap of width w_{gap} . However due to imperfections of the rf circuit (harmonics and spurious noise) the amplitude of the rf field within the gap is not strictly zero. In our experiments the spectral density of the rf power inside the gap is \sim 1000 times smaller than the spectral power density of the modes. The typical mean square amplitude of the in-plane rf oscillating magnetic field used in the "inverse" spectroscopy experiments is $\sqrt{\langle B_{rf}^2 \rangle} \approx 0.15$ mT, while the phases of the modes are chosen to minimize the crest factor so that the peak value is $B_{rf} \lesssim 0.3$ mT. In our experimental setup continuous rf excitation of such amplitude results in sample heating of less than 1 K.

The duration of the rf pulse for "inverse" spectroscopy $T_{rf} = 5.5$ s is chosen to be long enough to produce the steady-state population probability distribution of the nuclear spin states shown in Fig. 2(f). On the other hand for spectroscopy on phosphorus we use $T_{rf}=50$ ms which is shorter than the time required to completely erase nuclear polarization, and thus gives an unsaturated spectrum allowing broadening to be avoided. Both InP and InGaAs dots used in this work exhibit long nuclear spin decay times^{S1} $T_1 > 100$ s so that natural decay of nuclear polarization during rf excitation and probe pulse is negligible.

The "inverse" spectra (see Fig. 3) measured with σ^+ optical pumping were calculated as a difference $E_z^{gap} - E_z^{no\ gap}$ of the exciton Zeeman splitting E_z^{gap} measured using rf excitation with a gap in the spectrum at frequency ν and the splitting $E_z^{no\ gap}$ measured without the gap. Such correction allows NMR signal to be expressed as an absolute value of the hyperfine spectral shift. For σ^- pumping the difference was taken with the opposite sign ($E_z^{no\ gap} - E_z^{gap}$) to simplify comparison with spectra measured under σ^+ pumping. For "saturation" spectroscopy σ^+ pumping was used and the signal was calculated as $E_z^{no\ rf} - E_z^{rf}$, where E_z^{rf} ($E_z^{no\ rf}$) is the splitting measured

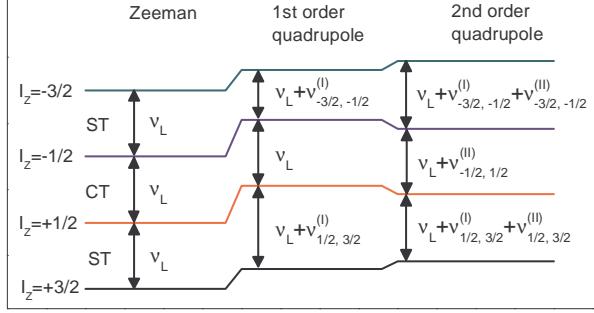


FIG. S4. Diagram of nuclear spin energy levels for the case of $I=3/2$ spin. Dipole transitions are shown with arrows. Zeeman interaction leads to equidistant shift of spin levels resulting in a degenerate transition at a Larmor frequency ν_L . Quadrupole interaction, which can be treated as a perturbation, leads to further shifts. The first order correction makes transition frequency $\nu_L + \nu_{I_z, I_z+1}^{(I)}$ dependent on the spins of the levels I_z and $I_z + 1$ thus removing the degeneracy. However the correction $\nu_{-1/2, 1/2}^{(II)}$ to the frequency of the central transition (transition between $-1/2$ and $1/2$ states) appears only in the second order.

with (without) rf excitation centered at frequency ν .

S3. NUCLEAR SPIN SPECTRUM IN THE PRESENCE OF STRAIN

Below we briefly summarize the effect of external fields on the nuclear spin spectrum. In magnetic field B_z along the Oz axis and in the presence of elastic strain, the Hamiltonian for a nuclear spin I can be written as^{S8}:

$$H_{nuc} = -h\nu_L I_z + H_Q, \quad (S1)$$

where $\nu_L = \gamma B_z / (2\pi)$ is Larmor frequency, h - Planck constant, γ is nuclear gyromagnetic ratio and H_Q describes interaction of the nuclear quadrupole moment with the electric field gradient (EFG), described by a second rank traceless tensor of the electrostatic potential second derivatives V_{ij} . In the frame $Ox'y'z'$ with the axes along the principal axes of V_{ij} :

$$H_Q = h\nu_Q [3I_{z'}^2 - I^2 - \eta(I_{x'}^2 - I_{y'}^2)] / 6, \quad (S2)$$

where $\nu_Q = \frac{3eQV_{z'z'}}{2I(2I-1)h}$ and $\eta = \frac{V_{x'x'} - V_{y'y'}}{V_{z'z'}}$ describe strength and deviation of the EFG from the axial symmetry, respectively^{S8}.

In the case of high magnetic field ($\nu_L \gg \nu_Q$) studied here the quadrupole interaction can be treated as a perturbation. The effect of external fields on nuclear spin level energies for the case of spin $I=3/2$ is shown in Fig. S4. Without quadrupole interaction frequencies of all transitions equal to ν_L determined by Zeeman energy. In the first order of ν_Q , the frequency of the $I_z' \leftrightarrow I_z' + 1$

transition, $\nu_L + \nu_{I'_z, I'_z+1}^{(I)}$, becomes dependent on I'_z . For the uniaxial EFG with the main axis along the external magnetic field this shift reads as $\nu_{I'_z, I'_z+1}^{(I)} = \nu_Q(I'_z + 1/2)$, i.e. $2I$ NMR lines are observed equally spaced by ν_Q . In the case of non-axial symmetry of the EFG ($\eta \neq 0$) or non-zero angle θ between EFG principle axis Oz' and magnetic field direction Oz , further changes in the transition frequencies are observed and the first order shift reads as:

$$\nu_{I'_z, I'_z+1}^{(I)} = \nu_Q(I'_z + 1/2)(1 + 3 \cos 2\theta - 2\eta \cos 2\phi \sin^2 \theta)/4, \quad (\text{S3})$$

where ϕ is the angle describing orientation of EFG axes with respect to Ozz' plane. For example, it follows from Eq. S3 that for $\eta = 0$ the first-order quadrupole shift can be canceled if strain axis deviates from the magnetic field by an angle $\theta \approx 54.7^\circ$.

However, the shift of the central transition $-1/2 \leftrightarrow 1/2$ appears only in the second order of ν_Q and can be written as:

$$\nu_{-1/2, 1/2}^{(II)} = \frac{2}{9} \frac{\nu_Q^2}{\nu_L} (I(I+1) - 3/4) G(\theta, \eta, \phi), \quad (\text{S4})$$

where $G(\theta = 0, \eta = 0, \phi) = 0$ and $-1 < G(\theta, \eta, \phi) < 1/2$ for all possible values of θ, η, ϕ [complete expressions for $G(\theta, \eta, \phi)$ can be found in Ref.^{S9}]. Thus for $\nu_L \gg \nu_Q$ the shift of the CT is much smaller than for the STs, resulting in a narrow central peak in the NMR spectra.

S4. CALCULATION OF THE NMR SIGNAL FOR "INVERSE" SPECTROSCOPY

Let us first consider "saturation" spectroscopy on quadrupolar nuclei subject to EFG when the spectrum of rf excitation has a single frequency component only. If the rf frequency ν is equal to the frequency of the transition between I'_z and $I'_z + 1$ states [$-3/2 \leftrightarrow -1/2$ in Figs. 2(a-c)], the populations of these spin levels are equalized [the dotted lines in Fig. 2(c)]. The populations of all other spin levels are not affected, and the total change of nuclear spin polarization P_N due to rf excitation is determined only by the contributions of I'_z and $I'_z + 1$ states. Taking the difference between the initial polarization $[(I'_z + 1)p_{I'_z+1} + I'_z p_{I'_z}]/I$ and the polarization after saturation of the transition $[(I'_z + 1) + I'_z] \times (p_{I'_z+1} + p_{I'_z})/(2I)$, we find the amplitude of the detected NMR signal as:

$$\Delta P_N^{sat} = (p_{I'_z+1} - p_{I'_z})/(2I). \quad (\text{S5})$$

By contrast in the "inverse" spectroscopy method [Figs. 2(d)-(f)] all spin states contribute to the NMR signal. For simplicity we consider the case of large EFG and narrow gap in the rf spectrum,

i. e. when the frequency of only one nuclear transition coincides with the gap. Calculations for a general case are bulky but straightforward. First we note that if the gap is not in resonance with any transitions then all nuclear polarization will be erased yielding the final polarization $P_N = 0$. If the gap is in resonance with the $I'_z \leftrightarrow I'_z + 1$ transition [$-3/2 \leftrightarrow -1/2$ in Figs. 2 (d-f)], i. e. this transition is not excited, then the equalization of populations takes place separately for two groups of spin levels: for states with $I_z \leq I'_z$ and for states $I_z \geq I'_z + 1$ [dotted lines in Fig. 2(f)]. This is because transfer of population induced by the rf field is allowed only between spin levels with I_z differing by ± 1 . For each group, the population probabilities of the spin levels after the rf pulse will be the average of their initial populations p_{I_z} . Thus non-zero polarization ΔP_N^{inv} will be retained:

$$\Delta P_N^{inv} = \frac{I'_z - I}{2I} \sum_{k=-I}^{I'_z} p_k + \frac{I + I'_z + 1}{2I} \sum_{k=I'_z+1}^I p_k. \quad (S6)$$

The initial polarization of the nuclear spins created via the hyperfine interaction with the optically pumped spin-polarized electrons can be expressed in terms of the electron spin temperature T_e , assuming that the nuclear spin populations p_{I_z} follow a Boltzman distribution. In large magnetic fields when $\nu_L \gg \nu_Q$, the energies of the nuclear spin levels are approximately proportional to I_z and the initial populations can be described as^{S10}:

$$p_{I_z} = Z^{-1} \exp(I_z \beta), \\ \beta = \left(\frac{E_{eZ}}{k_B T} - \frac{E_{eZ}}{k_B T_e} \right), \quad (S7)$$

where Z is the normalization factor, k_B - Boltzman constant, E_{eZ} - the electron Zeeman splitting. β describes the dynamic nuclear polarization occurring as a result of deviation of the electron spin temperature T_e from the bath temperature T due to optical orientation of the electrons. In the studied case $|T_e| \ll T$ and the term $E_{eZ}/(k_B T)$ can be neglected.

Using the Boltzman population distribution of Eq. S7 we can calculate the sums in Eqs. S5 and S6 and obtain the following expressions for the signal amplitudes for both "saturation" and "inverse" NMR:

$$\Delta P_N^{sat,B} = \frac{[e^{(I'_z+1)\beta} - e^{I'_z\beta}]}{2I} \frac{\sinh(\beta/2)}{\sinh[(2I+1)\beta/2]}, \\ \Delta P_N^{inv,B} = \frac{(I - I'_z) + (I + I'_z + 1)e^{(2I+1)\beta} - (2I + 1)e^{(I+I'_z+1)\beta}}{2I[e^{(2I+1)\beta} - 1]}. \quad (S8)$$

It is useful to consider several practical cases. For example, the amplitude of the $-1/2 \leftrightarrow 1/2$ central transition (CT) signal is obtained from Eqs. S8 by substituting $I'_z = -1/2$. For a given

I , the CT NMR signal ΔP_N becomes a function of β and it can be easily derived that for any β , "inverse" spectroscopy yields a signal enhancement of at least $\Delta P_N^{inv,B}/\Delta P_N^{sat,B} > (I+1/2)^3$. For example, for $I = 9/2$ spin (indium) it is $\Delta P_N^{inv,B}/\Delta P_N^{sat,B} > 125$. Since the CT exhibits a narrow line in the NMR spectrum it is much easier to detect even in the presence of large quadrupole effects. Thus the use of "inverse" NMR greatly enhances the sensitivity for detection of even small amounts of quadrupole isotopes, in particular with large I . For the smallest half-integer quadrupole nuclear spin $I = 3/2$, "inverse" NMR for the CT still leads to a signal enhancement of $\Delta P_N^{inv,B}/\Delta P_N^{sat,B} > 8$. For the satellite transitions (STs) the sensitivity of "inverse" NMR reduces with increasing I'_z . However, even for the most split-off transitions $-I \leftrightarrow -I+1$ and $I-1 \leftrightarrow I$, the enhancement is $\Delta P_N^{inv,B}/\Delta P_N^{sat,B} > 9$ for $I = 9/2$ and > 3 for $I = 3/2$.

It is also useful to compare NMR sensitivity in strained and unstrained structures. In the absence of quadrupole effects all nuclear transitions have the same frequencies, and thus for both "saturation" and "inverse" techniques the NMR signal will be given by the initial polarization degree P_N . Using Eqs. S7 and S8 we can calculate the ratio of the CT NMR signal ΔP_N in the presence of EFG and the total signal P_N for zero EFG. For "inverse" NMR we find that for all β this ratio is $\Delta P_N^{inv,B}/P_N > 0.55$ for $I = 9/2$ ($\Delta P_N^{inv,B}/P_N > 0.66$ for $I = 3/2$), implying that sensitivity in the strained structures is only two times smaller compared to the structures with zero quadrupole effect. By contrast, for saturation spectroscopy, non-zero EFG results in suppression of NMR signal particularly strong for nuclei with large spin: we find that at least $\Delta P_N^{sat,B}/P_N < 0.0061$ for $I = 9/2$ and $\Delta P_N^{sat,B}/P_N < 0.1$ for $I = 3/2$.

S5. ESTIMATION OF THE CHEMICAL COMPOSITION OF THE DOTS

This section presents an experimental method and numerical analysis enabling estimation of Ga and In intermixing within the volume of the electron wavefunction in a QD. We use a long rf pulse leading to selective (and complete) depolarization of the i -th isotope, thus enabling a selective measurement of the corresponding hyperfine shift (the change in the exciton spectral splitting) $\Delta E_{Z,i}$. The $\Delta E_{Z,i}$ can be expressed via the nuclear polarization degree $P_{N,i}$ of the i -th isotope as:

$$\Delta E_{Z,i} = \rho_i A_i I P_{N,i}, \quad (S9)$$

where ρ_i is the relative concentration of that isotope and A_i is its hyperfine constant^{S8}. For InP, where the contribution of ^{115}In dominates, the hyperfine constant has been measured experimentally^{S11}: $A_{^{115}\text{In}} \approx 47 \text{ } \mu\text{eV}$. Using this value, and neglecting variation of electron

density between gallium and indium sites, we can estimate the hyperfine constant for ^{69}Ga as $A_{^{69}\text{Ga}} = A_{(^{115}\text{In})} \frac{\mu_{(^{69}\text{Ga})}}{\mu_{(^{115}\text{In})}} \frac{9/2}{3/2} \approx 51 \mu\text{eV}$, and similarly for ^{71}Ga as $A_{^{71}\text{Ga}} \approx 65 \mu\text{eV}$. We also take into account that the two gallium isotopes have natural abundances $\sigma_{^{69}\text{Ga}} \approx 0.6$ and $\sigma_{^{71}\text{Ga}} \approx 0.4$. By introducing the total gallium concentration ρ_{Ga} we can write $\rho_{^{69}\text{Ga}} = \sigma_{(^{69}\text{Ga})} \rho_{\text{Ga}}$, $\rho_{^{71}\text{Ga}} = \sigma_{(^{71}\text{Ga})} \rho_{\text{Ga}}$. Since ^{115}In and ^{69}Ga have similar NMR frequencies, we can only measure their combined Overhauser shift $\Delta E_{Z,^{69}\text{Ga}} + \Delta E_{Z,^{115}\text{In}}$. The Overhauser shift for ^{71}Ga , $\Delta E_{Z,^{71}\text{Ga}}$, is measured separately. Finally, the nuclear spin polarization for each isotope $P_{N,i}$ can be calculated using the Boltzman distribution (Eq. S7) and thus expressed in terms of polarization parameter β for a given spin I . Using Eq. S9 we can write the following system of equations for ρ_{Ga} , ρ_{In} and β :

$$\begin{aligned} \Delta E_{Z,^{69}\text{Ga}} + \Delta E_{Z,^{115}\text{In}} &= \frac{9}{2} \rho_{\text{In}} A_{(^{115}\text{In})} P_{N,(^{115}\text{In})} + \frac{3}{2} \sigma_{(^{69}\text{Ga})} \rho_{\text{Ga}} A_{(^{69}\text{Ga})} P_{N,(^{69}\text{Ga})}, \\ \Delta E_{Z,^{71}\text{Ga}} &= \frac{3}{2} \sigma_{(^{71}\text{Ga})} \rho_{\text{Ga}} A_{(^{71}\text{Ga})} P_{N,(^{71}\text{Ga})}, \\ \rho_{\text{Ga}} + \rho_{\text{In}} &= 1. \end{aligned} \quad (\text{S10})$$

For InP/GaInP QDs we measured the following values of the hyperfine shifts: $\Delta E_{Z,^{115}\text{In}} + \Delta E_{Z,^{69}\text{Ga}} \approx 120 \mu\text{eV}$ and $\Delta E_{Z,^{71}\text{Ga}} \approx 8 \mu\text{eV}$. Solving Eq. S10 we find $\rho_{\text{Ga}} \approx 35\%$, $\rho_{\text{In}} \approx 65\%$ implying significant penetration of the electron wavefunction into the GaInP barrier and/or diffusion of gallium into the dot. We also find $\beta \approx 0.8$ corresponding to the average electron spin of $|\langle s_z \rangle| \approx 0.2$. For InGaAs quantum dots we assume the same values of hyperfine constants A_i . Using the measured shifts $\Delta E_{Z,^{115}\text{In}} + \Delta E_{Z,^{69}\text{Ga}} \approx 56 \mu\text{eV}$ and $\Delta E_{Z,^{71}\text{Ga}} \approx 18 \mu\text{eV}$, we find $\beta \approx 0.8$ and, as expected from peaks amplitudes of the NMR spectrum in Fig. 3(c), a much lower concentration of indium $\rho_{\text{In}} \approx 20\%$. For both types of quantum dots we find very similar high degrees of optically pumped nuclear spin polarization: $P_{N,(^{115}\text{In})} \approx 0.8$ and $P_{N,(^{71}\text{Ga})} \approx 0.6$.

There are two possible scenarios resulting in relatively low average concentration of indium ($\rho_{\text{In}} \approx 20\%$) in InGaAs QDs revealed by the NMR measurements: (i) the nominal InAs QD contains significant amount of gallium due to diffusion during the growth process, or (ii) the dot itself consists mainly of indium but has a small size resulting in weak charge localization and significant penetration of electron wavefunction into the GaAs barrier. In both cases QDs will have a larger band-gap compared to the large-size InAs dots. This is indeed observed in the experiment: the wavelength of the ground state exciton recombination in the studied dots is $\lambda \sim 915 \text{ nm}$ compared to $\lambda > 1000 \text{ nm}$ in large indium-abundant dots.

S6. ESTIMATION OF STRAIN IN A QD

Elastic strain is described by a second-rank symmetric tensor ϵ_{ij} . The resulting electric field gradient (EFG) V_{ij} can be related to ϵ_{ij} via a fourth-rank tensor S_{ijkl} as^{S12}

$$V_{ij} = \sum_{k,l} S_{ijkl} \epsilon_{kl}, \quad (i, j, k, l = x, y, z). \quad (\text{S11})$$

In a crystal with cubic symmetry there are only 3 independent components denoted as S_{11} , S_{12} and S_{44} . The symmetry relation $S_{12} = -S_{11}/2$ is usually used to account for the zero trace of the V_{ij} tensor, leaving only 2 independent components^{S12}. Thus Eq. S11 can be rewritten as

$$\begin{aligned} V_{ii} &= S_{11}(\epsilon_{ii} - (\epsilon_{jj} + \epsilon_{kk})/2), \quad i \neq j \neq k \\ V_{ij} &= 2S_{44}\epsilon_{ij}, \quad i \neq j. \end{aligned} \quad (\text{S12})$$

It follows from Eq. S12 that isotropic (hydrostatic) strain $\epsilon_h = \epsilon_{xx} + \epsilon_{yy} + \epsilon_{zz}$ produces no EFG, while biaxial (including uniaxial) and shear strains give rise to quadrupole shifts of NMR resonances.

For uniaxial ($\epsilon_{xx} = \epsilon_{yy}$) strain $\epsilon_b = \epsilon_{zz} - (\epsilon_{xx} + \epsilon_{yy})/2$ along the direction of the applied magnetic field, the frequency shift of the $1/2 \leftrightarrow 3/2$ transition from the CT reads as $\nu_Q = \frac{3eQS_{11}\epsilon_b}{2hI(2I-1)}$, where Q is the quadrupole moment, h is the Planck constant. For the studied isotopes the quadrupole moments are: $Q(^{69}\text{Ga}) \approx 0.17$, $Q(^{71}\text{Ga}) \approx 0.10$, $Q(^{75}\text{As}) \approx 0.31$ and $Q(^{115}\text{In}) \approx 0.8$ barn (1 barn = 10^{-28} m²). For ⁷¹Ga in InGaAs dots the maximum $\nu_Q \sim 2.5$ MHz can be estimated from the width of the sidebands in the NMR spectrum in Fig. 3(e). Using the value $S_{11} \approx 2.7 \times 10^{22}$ V/m² measured for gallium in bulk GaAs^{S12} we estimate $|\epsilon_b| \approx 6\%$.

In InP dots we use NMR on ¹¹⁵In satellite transitions to estimate strain magnitude. According to Eq. S8, the amplitude of the "inverse" NMR signal from the satellite transition $I'_z \leftrightarrow I'_z + 1$ decreases with increasing spin $|I'_z|$, leading to insufficient signal for large $|I'_z|$ and unreliable estimation of the maximum quadrupole shift. This is overcome in an additional experiment, where long broadband rf pulse (without the gap) centered at the frequency of the indium CT transition is used to erase polarization of indium. The total width of the excitation spectrum w_{exc} is varied. We find that the magnitude of the erased nuclear polarization initially increases with w_{exc} and saturates at a constant level at $w_{exc} \approx 20$ MHz. This allows the maximum shift of the $7/2 \leftrightarrow 9/2$ transition frequency to be estimated as ~ 10 MHz, which is also equal to $4\nu_Q$. Using then $S_{11} \approx 5.9 \times 10^{22}$ V/m² for indium in InP we estimate the maximum strain as $|\epsilon_b| \approx 5\%$.

Elastic strain also affects the CT frequency. Using $\nu_Q \approx 2.5$ MHz derived for ¹¹⁵In we find that the shift of ¹¹⁵In resonance according to Eq. S4 can be as large as $\nu_{-1/2,1/2}^{(II)} \approx -0.65$ MHz at

$\nu_L \approx 49.7$ MHz. For example, in the case of $\eta = 0$ and angle $\theta \approx 54.7^\circ$ corresponding to zero shift of ST bands the second-order shift of the CT is $\nu_{-1/2,1/2}^{(II)} \approx -0.25$ MHz. On the other hand in experiment [Fig. 3(b)] we observe shifts only on the order of ± 50 kHz compared to the frequency ν_{In} in unstrained InP¹³. This suggests that the deviation between the strain axis and external field (characterized by θ) as well as non-axial symmetry of EFG (characterized by η) are small. Thus, the most likely reason for the inhomogeneous distribution of ST shifts is the variation of ν_Q within the dot volume caused by variation of the biaxial strain magnitude ϵ_b . In particular, non-zero amplitude of ST bands at CT frequency observed in Fig. 3(a) for ¹¹⁵In can be explained by complete biaxial strain relaxation at the center of the dot^{S14,S15} resulting in $\nu_Q = 0$. For ⁷⁵As nuclei large EFG can result not only from elastic strain but also from electric fields created by random substitution of gallium atoms by indium. This may explain the further broadening of ⁷⁵As CT transition.

We note a significant difference in the asymmetry of the NMR spectra in Figs. 3 (e,f): for ⁷⁵As the low (high) frequency ST band is enhanced for $\sigma^{-(+)}$ pumping while for indium and gallium isotopes this asymmetry is reversed. The sign of the asymmetry is determined by the relative signs of Zeeman and quadrupole contributions to the nuclear Hamiltonian Eq. S1. Since all isotopes of InGaAs have positive gyromagnetic ratios γ and positive quadrupole moments Q , the opposite asymmetries of the spectra can be attributed to the opposite signs of the electric field gradients $V_{z'z'}$ (see Eq. S2) experienced by nuclei of anions (As) and cations (Ga or In).

S7. SPIN COHERENCE IN THE NUCLEAR SPIN ENSEMBLE SUBJECT TO INHOMOGENEOUS STRAIN

This section details the experimental procedure and the model used for analysis of the dependence of the nuclear polarization dynamics in InP dots on the spacing between the modes in the broad-band rf excitation. The dynamics of the rf-induced nuclear spin polarization decay is measured using a pump-probe technique. Initially, nuclear spins are polarized optically. Then an rf-pulse of duration T_{rf} is applied after which the nuclear spin polarization is probed optically by measuring the exciton Zeeman splitting E_z . The spectrum of the rf excitation (without the gap) consists of a large number of spectral modes with equal spacing w_m and with equal amplitudes B_m changed as $B_m \propto \sqrt{w_m}$ to keep the total power of the rf pulse constant (See Fig. 4). The spectral range 44-47.5 MHz of the rf excitation is kept fixed and corresponds to satellite transitions of In nuclei [Fig. 3(a)]. The experimental dependences of the Overhauser shift on the rf excitation time

T_{rf} are shown with symbols in Fig. S5(a) for two different mode spacings w_m of the rf-excitation spectrum. As seen, the increase of w_m from 0.2 to 4 kHz results in a significant increase of the time required to equalize populations of the nuclear spin levels coupled by the rf field. We use exponential fitting with a time constant $1/R_{rf}$ to quantify the rate R_{rf} of rf induced depolarization. The resulting dependence of R_{rf} on w_m is shown in Fig. 4(b) and is repeated with symbols in Fig. S5(b).

We now present in full the model that allows the study of coherence properties of nuclear spins using nuclear spin dynamic measurements. We start by noting that, in high external magnetic fields, nuclear spins are characterized by very long T_1 times^{S1} exceeding 100 s, arising from suppressed energy relaxation leading to low probability of spin flips. Intrinsic linewidths of NMR transition correspond to much shorter times T_2 determined by energy-conserving decoherence of transverse components of nuclear spins. This decoherence is induced by random dipole-dipole fields of other nuclei, and is characterized by the autocorrelation function which we choose in the form:

$$g(t) = \frac{1}{1-\alpha} \exp[-t/T_2] - \frac{\alpha}{1-\alpha} \exp[-t/(\alpha T_2)], \quad (\text{S13})$$

where $\alpha \ll 1$ is a dimensionless parameter. For $\alpha = 0$ this corresponds to an exponential correlation function with the relaxation time T_2 derived in the general theory of relaxation caused by fluctuations^{S16}. The addition of the second term in Eq. S13 allows the condition $g'(0) = 0$ required by time reversal symmetry to be satisfied. The lineshape of the nuclear spin transition is found as the Fourier transform of $g(t)$:

$$\tilde{g}(\nu) = \frac{T_2(1+\alpha)}{1 + (1+\alpha)^2(2\pi\nu)^2 T_2^2 + \alpha^2(2\pi\nu)^4 T_2^4}. \quad (\text{S14})$$

As expected for $\alpha = 0$ this expression corresponds to a Lorentzian lineshape.

For a nuclear spin transition between I'_z and $I'_z + 1$ states at a frequency ν_{nuc} , a small amplitude (non-saturating) rf field will result in depolarization, which can be described by the differential equation for the population probabilities $d(p_{I'_z+1} - p_{I'_z})/dt = -W \times (p_{I'_z+1} - p_{I'_z})$. For broadband rf excitation consisting of discrete modes with frequency spacing w_m , each inducing an equal magnetic field B_m , depolarization rate W is given by:

$$W(\nu_{nuc}) = B_m^2 \sum_{k=0}^N \tilde{g}(\nu_{nuc} - \nu_0 - k \times w_m), \quad (\text{S15})$$

where the summation goes over all modes of the rf field with frequencies $\nu_k = \nu_0 + k \times w_m$ (ν_0 is the frequency of the first spectral mode). Since the total width of the rf band is much larger than w_m or the nuclear spin transition width w_{nuc} , the summation in Eq. S15 can be extended to $\pm\infty$.

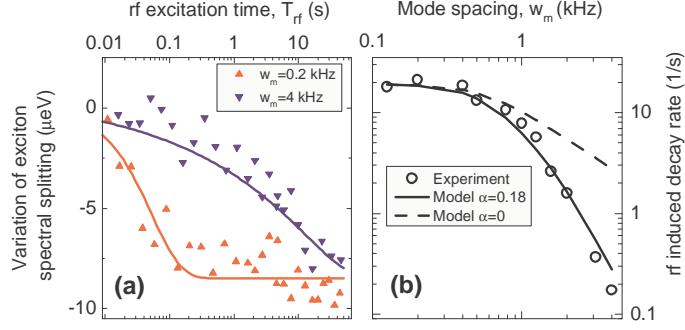


FIG. S5. (a) Experimentally measured nuclear spin polarization decay (symbols) for the rf-excitation mode spacings $w_m = 0.2$ kHz and 4 kHz. Nuclear polarization is calculated as a difference of exciton spectral splittings E_Z measured after rf-pulse with duration T_{rf} and before this pulse. Lines show model fitting. (b) Dependence of rf induced nuclear depolarization rate R_{rf} on the mode spacing w_m . Values extracted using exponential fitting of the experimental decay curves are shown with symbols. The dashed (solid) line shows results of calculations using the presented model for a Lorentzian (non-Lorentzian) lineshape $\alpha = 0$ ($\alpha \approx 0.18$).

For each individual pair of nuclear spin states, the rf field will induce an exponential decay of polarization. However, the QD contains a large number of nuclear spins with randomly distributed transition frequencies ν_{nuc} . Thus, in order to calculate the dynamics of the total nuclear polarization, we need to average over all possible values of ν_{nuc} . Since the spectrum of the rf band is a periodic function (i.e. the modes are equally spaced), such averaging can be done over one period. We also assume a uniform distribution of the nuclear transition frequencies ν_{nuc} . Thus, the following expression is obtained for the time dependence of the difference between the current and initial nuclear spin polarization, describing the dynamics of rf-induced depolarization:

$$P_N(t) - P_N(0) = -P_N(0) + P_N(0) \int_0^{w_m} \exp \left(-tB \sum_{k=-\infty}^{\infty} \tilde{g}(\nu_{nuc} - k \times w_m) \right) d\nu_{nuc}, \quad (S16)$$

where $B^2 \propto B_m^2/w_m$ is proportional to the spectral density of the total rf field power, which is kept constant in our experiment when w_m is varied.

Using Eq. S16 we can fit nuclear spin decay curves measured for different values of w_m . In Fig. S5(a) this is demonstrated for $w_m = 0.2$ and 4 kHz. From the fitting of the whole set of decay curves measured with rf excitation in the spectral range 44-47.5 MHz for different w_m we find good agreement with experiment for a nuclear spin dephasing time $T_2 \approx 2.5$ ms and lineshape parameter $\alpha \approx 0.18$. The same magnitudes of these parameters are obtained from fitting the data of a similar experiment but for an rf excitation band in resonance with a different section of the satellite transitions at 47.0-49.0 MHz.

We can now use the results of the fitting to analyze coherent dynamics of indium nuclear spins. We start by noting that for small w_m all nuclear spin transitions are excited with nearly the same efficiency (similar to a white-noise excitation) resulting in an overall decay close to exponential. For larger spacing, the model given by Eq. S16 significantly deviates from the exponential decay: at the initial stage those transitions which are in resonance with the rf modes quickly become depolarized, whereas the decay is significantly slower for off-resonance transitions. For the analysis of the lineshape parameter α we characterize the rate of the decay given by Eq. S16 using the time $t_{1/2}$ where nuclear polarization decreases to 1/2 of the initial value. The decay rate can be estimated as $R_{rf} = \log(2)/t_{1/2}$ (in the limit of small w_m it coincides with exponential decay rate). The dependence $R_{rf}(w_m)$ calculated in this way from Eq. S16 with parameters obtained from the fitting ($T_2 \approx 2.5$ ms and $\alpha \approx 0.18$) is shown in Fig. S5(b) with a solid line. Calculation with the same T_2 but for $\alpha=0$ is shown with a dashed line.

It can be seen that in the limit of small w_m decay rate does not depend on α for both $\alpha=0$ and $\alpha=0.18$. However, at larger mode spacing modeling using pure Lorentzian lineshape fails to describe the experiment (i.e. it is impossible to fit simultaneously all decay curves corresponding to different w_m using Eq. S16 with $\alpha = 0$). This deviation is described by the fourth order term $\propto \nu^4$ in the denominator of Eq. S14. This term is responsible for much smaller depolarization rate at large detunings $\nu \gg 1/(\pi T_2)$ in case of non-Lorentzian lineshape. At large mode spacing w_m most nuclear spin transitions are excited only via their "wings" (i. e. at large ν), and thus the effect of non-Lorentzian shape becomes more pronounced as seen in Fig. S5(b). Strong deviation of the nuclear transition lineshape from Lorentzian function reveals non-exponential character of nuclear spin decoherence (described by Eq. S13 in our model) and demonstrates the potential of the presented technique for deeper understanding of the spin coherence of quadrupole nuclei.

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